

Opportunities and challenges of Lithium Manganese Iron Phosphates as positive electrode materials for Lithium Ion batteries

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Much attention is paid to the carbon coated LiFePO₄ material for large format Lithium Ion batteries because of the large availability of iron raw materials, the excellent safety properties and the high charge/discharge rate capability of the related lithium ion batteries (1-2). However, there is a strong need for high energy density for automotive applications.

The carbon coated lithium manganese phosphate offers in principle similar safety behaviour but a larger energy density because of its larger voltage (4.1 V vs. Li) compared to the iron system (3.45 V vs. Li). The synthesis of electroactive C-LiMnPO₄ proved to be difficult (3-4). Downsizing this material and substitution of manganese by iron has been shown effective to enhance the reversible capacity (3-6).

Samples of LiMn_{1-x}Fe_xPO₄ (0 ≤ x ≤ 1) positive electrode materials were prepared by a precipitation process (7). Their electrochemical properties were tested in laboratory lithium cells and compared to those of Süd Chemie's LiFePO₄.

A significant improvement of energy density versus LiFePO₄ has been proven for the C-LiMn_{0.70}Fe_{0.30}PO₄ as shown in Figure 1. Moreover, a good discharge rate capability could be demonstrated for C-LiMn_{0.70}Fe_{0.30}PO₄ electrodes (140 mAh/g at 5C) when the batteries are slowly and completely charged as reported in Figure 2.

Three main characteristics of the C-LiMn_{1-x}Fe_xPO₄ batteries were observed during the electrochemical tests at RT:

- The battery charge conditions have a large impact on the achieved discharge capacity and energy density, especially when the manganese content in the olivine material approaches 100%, as shown in Figure 3.
- A significant polarisation in the 4V region is observed at discharges rates > 1C.
- The length of the 4V pseudo plateau decreases upon cycling or after a rate capability test, while the specific discharge capacity remains quasi constant.

The electrochemical characteristics of C-LiMn_{1-x}Fe_xPO₄ are compared to those of C-LiFePO₄ and the reasons for the lower activity of the 4V region for the manganese based materials will be discussed during the meeting.

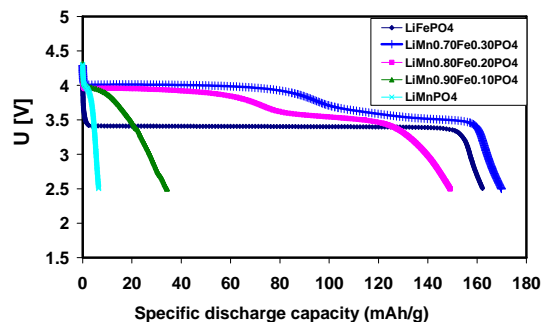


Figure 1: First specific discharge capacity of Süd Chemie's C-LiMn_{1-x}Fe_xPO₄ electrodes (x = 0.0; 0.1; 0.2; 0.3; 1.0) measured at 25°C in EC: DMC 1:1/ 1M LiPF₆ electrolyte. The charging procedure was C/10 followed by a CV step until C/100.

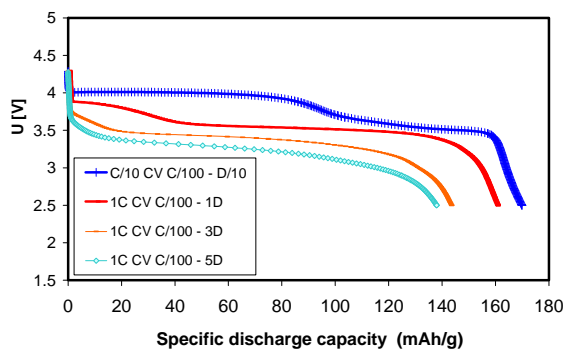


Figure 2: Specific discharge capacity of a Süd Chemie's C-LiMn_{0.70}Fe_{0.30}PO₄ electrode measured at various rates during cycling at 25°C in EC: DMC 1:1/ 1M LiPF₆. The batteries were charged in CCCV mode.

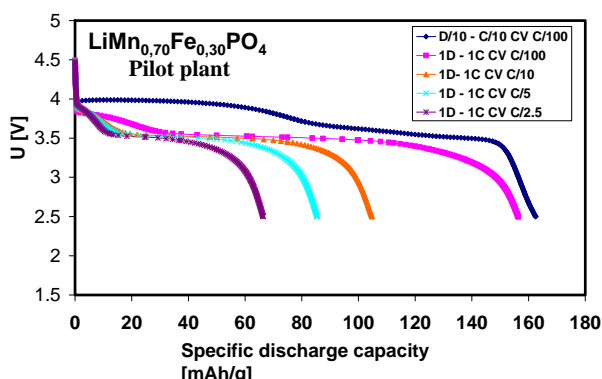


Figure 3: Influence of charging conditions on the discharge capacity for a Süd Chemie's C-LiMn_{0.70}Fe_{0.30}PO₄ electrode measured at 25°C in EC: DMC 1:1/ 1M LiPF₆. The lithium batteries were charged in CCCV mode until various current limits.

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